Recent Trends in Ambient Sulfate Aerosol

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Summary

Sulfur dioxide emissions in the United States have decreased since the middle 1990s. Several monitoring networks provide data that can be used to examine trends in ambient sulfur levels. Two networks—CASTNet (EPA) and IMPROVE (federal land managers)—have different objectives and measurement protocols but provide information on particulate sulfate. The CASTNet network also provides data on gaseous SO_2. A recently reported analysis of CASTNet data found an apparent discrepancy between annual trends in SO_2 and sulfate that the authors were unable to resolve. The study reported here analyzes both the CASTNet and IMPROVE data sets in terms of seasonal trends in sulfur, and compares them with SO_2 emissions trends.

The nature of sulfate is such that these networks should produce data that are roughly comparable. The largest problem is the lower temporal coverage of the IMPROVE data. The low sampling frequency results in uncertainty in seasonal average concentrations and temporal trends. This fact, and the greater spatial coverage provided by the CASTNet data across the eastern U.S., are the primary reasons why most emphasis in placed on the CASTNet trends. The IMPROVE data are examined to identify areas of corroboration and disagreement with the CASTNet findings. Another difficulty with comparing the data sets is that the greatest number of IMPROVE stations were not operational until around 1992, whereas the majority of CASTNet sites were operational by 1988. Thus, trends are analyzed for two intervals, 1988-1999 and 1992-1999, to maximum the time interval while also enabling comparisons between the two networks for the period when most data are available.

<u>CASTNet Seasonal Trends</u> – Mean seasonal trends were computed from a least-squares fit of seasonal average concentrations across all years. The average trend is the slope of the regression equation. Generally, CASTNet sulfate levels declined over the eastern U.S. during 1988-1999 for all seasons. This was not necessarily true for the 1992-1999 interval, however. Spring sulfate showed declines for both intervals, but some regions (especially the Southeast) experienced sulfate increases during 1992-1999 for summer and autumn. In contrast sulfur dioxide levels generally decreased everywhere (except in the Southwest) during both intervals. This decrease is consistent with trends in SO_2 emissions. The apparent sulfur trends discrepancy could indicate a significant weakness in our scientific understanding of sulfur chemistry. An alternate explanation is suggested by the differences in trends found for spring versus summer and autumn. The spring trends, regardless of year interval, are consistent with SO_2 trends. The differential behavior found for summer and autumn could be caused by interannual variations in weather patterns that influence sulfate formation and removal processes. This would explain why sulfate increases occurred in autumn during 1992-1999 in places like southeast Pennsylvania, an area downwind of the Ohio River valley that contains the highest concentration of SO_2 sources and had the largest SO_2 emission reductions.

<u>CASTNet versus IMPROVE</u> – Difficulties comparing trends defined by the two PS monitoring networks are primarily attributable to the larger uncertainty associated with average seasonal levels determined from the IMPROVE data. Uncertainty, due to incomplete sampling, in CASTNet PS tendencies is negligible because of a high degree of data completeness. The low temporal coverage results in uncertainty that can be estimated using a statistical resampling technique. Applying this technique to the IMPROVE data, even while adjusting the resampling method to take advantage of autocorrelation in the data, indicates that, for most sites, trends cannot be determined with a high level of confidence. Even so, there are similarities in the estimated temporal tendencies.

Despite the lower level of certainty, IMPROVE sites were more likely to experience decreasing sulfate tendencies in winter and spring than summer and fall. This is consistent with the findings for the CASTNet data. The largest PS declines were computed for the same CASTNet regions (generally the Ohio Valley and surrounding areas) found to have the greatest sulfate improvements. Differences in the direction of changes at CASTNet and IMPROVE sites were more likely due to the differences in locations where monitoring was done. IMPROVE tendencies were smaller than those from the CASTNet data in part because of an artifact of the resampling technique that was applied to the former data.

Site Comparisons – CASTNet and IMPROVE spring PS time series were compared for Shenandoah National Park in Virginia. The two sites are only a few kilometers apart. Elevation differences were removed by adjusting all concentrations to reflect standard temperature and pressure. Both time series indicate downward tendencies in sulfate. The overall change in CASTNet PS was greater than that for IMPROVE. IMPROVE data are represented by showing the seasonal averages (without resampling), the resampled averages, and the estimated uncertainties in the seasonal averages. CASTNet values all fall within the 95% confidence interval for the resampled IMPROVE averages. Thus, the two time series cannot be statistically distinguished from one another.

A CASTNet site (station PNF), located is western North Carolina, was compared to the IMPROVE site (station GRSM) 180 km away in the Great Smoky Mountains. Although more separated than the Shenandoah sites, both are relatively elevated compared to surrounding terrain (PNF: 1219 m; GRSM: 815 m). PNF is northeast of GRSM with a PS time series that begins in 1989. GRSM monitoring using current IMPROVE protocols began in 1988. PNF values tend to be greater than those at GRSM. The average 1989-1999 change in summer PS at PNF was -0.05 $\mu g\ m^{-3}\ yr^{-1}$. During 1988-1999, GRSM PS changed by an average of +0.03 $\mu g\ m^{-3}\ yr^{-1}$. The difference is due to the 1988 data at GRSM. Subtracting 1988 would result in a near-zero net change in PS at GRSM for the 1989-1999 interval. For the 1992-1999 interval, PNF PS increased an average of 0.10 $\mu g\ m^{-3}\ yr^{-1}$ while GRSM remained nearly unchanged at -0.01 $\mu g\ m^{-3}\ yr^{-1}$.

Conclusions – CASTNet seasonal average PS tendencies since 1988 show a distinctive pattern of decline across the eastern U.S. for all seasons. Tendencies since 1992 have been more variable. In some regions, tendencies were similar to those during 1988-1999. However, across the Southeast PS tendencies were upward for summer and autumn, and were also upward in the east-central U.S. in autumn. Tendencies computed from IMPROVE data showed similar directions in changes even though confidence in the changes was smaller. Regional increases in PS levels for summer and autumn periods during 1992-1999 were inconsistent with changes that were believed to have occurred in SO_2 emissions. The unexpected behavior could be explained by changes in seasonal weather patterns during 1992-1999. Such weather pattern shifts may not have affected other seasons, especially spring, as much as summer and autumn and may not have been large enough to have influenced PS changes during the longer 1988-1999 interval. Comparisons between selected pairs of CASTNet and IMPROVE sites in close proximity revealed that the data time series are not always in good agreement.